

MICROCRYSTALLINE CELLULOSE

The oldest polymer finds new industrial uses

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From the day that the term "hydrocellulose" was first coined in 1875 until the present, treatment of cellulose with acids has been considered the wrong direction to go. By going in this direction (and making a fortunate detour) we have been rewarded with a view of an entirely new area of cellulose chemistry.

Uses of cellulose have always depended upon—and been largely limited by—its fibrous nature. In this new area, cellulose is a colloid, with all of the implied possibilities. Industrial uses are promising for:

- Flour. Nonfibrous, free flowing, absorbent, with extremely high surface area
- Compacted pellets. Hard, heat resistant, absorbent, inert
- Structural materials. Hard, insulating materials, resistant even to an oxyacetylene torch
- Gels and creams. Smooth, opaque, stable, fat-like but noncaloric
- Cellulose derivatives. Produced with greater ease and economy, and in new colloidal form

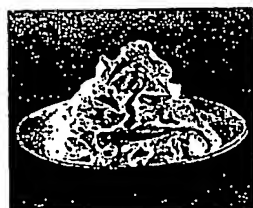
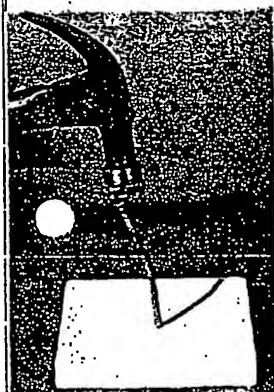
Production of the flour form is the basic step in manufacture of these types of microcrystalline cellulose. Severe acid hydrolysis removes the hinges of amorphous cellulose which link the naturally occurring microcrystals, yielding cellulose at the so-called "level-off degree of polymerization" or "D.P. cellulose." The microcrystals are freed from their fibrous, packed structure by mechanical shearing, performed in a water slurry. This is the novel step which determines the unique character of this cellulose. Drying then produces a flour of colloidal size.

The flour can be redispersed with water to form thick gels or thinner creams. It can be compacted into tablets or to large structural sheets. An entirely different, denser structural sheet results when a thick gel is dried.

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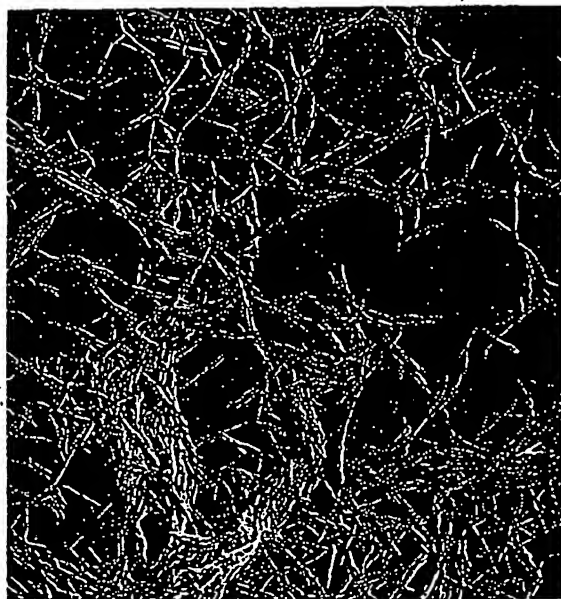
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Appreciation is extended to F. H. Reichel, Jr., Director of Corporate Research, under whose direction microcrystalline cellulose was advanced to commercial production.

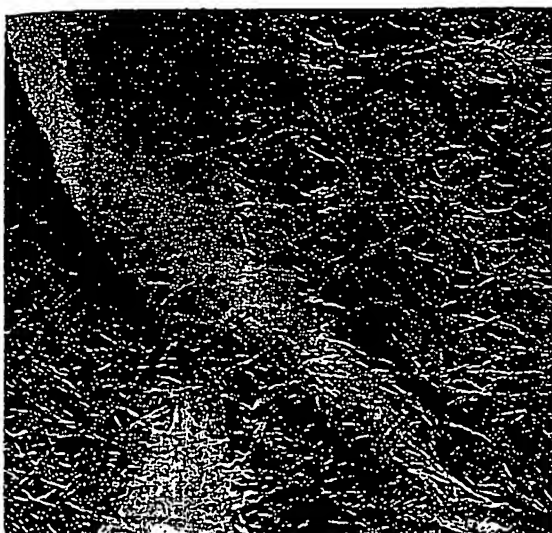




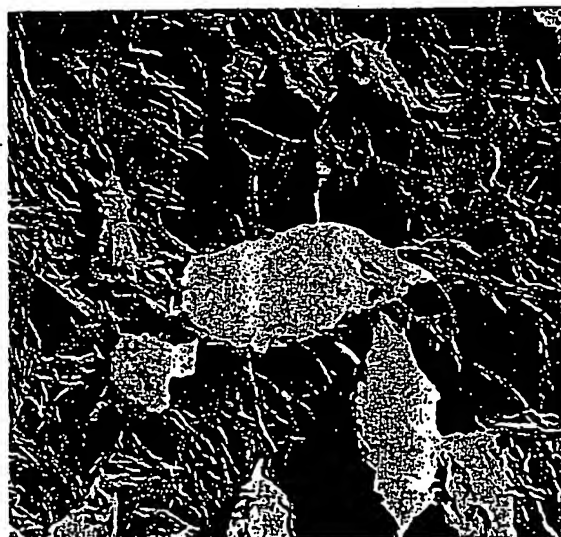
A



B



C



D

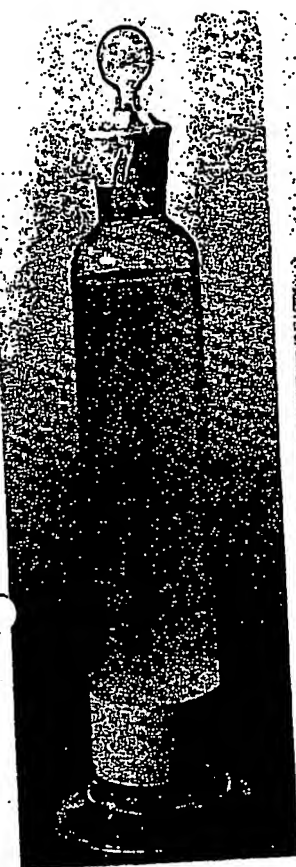
MICROCRYSTALS OF CELLULOSE ARE BUILDING-BLOCKS

D.P. microcrystalline cellulose is capable of forming architectural patterns entirely different from any previously known structure.

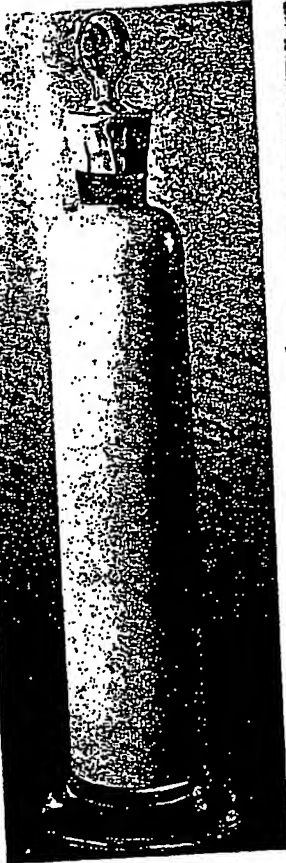
In natural cellulose the microcrystals are packed tightly in the fiber direction in a compact structure resembling bundles of wooden matchsticks placed side-by-side (A, above). Unhinging the interconnecting chains by acid treatment does not destroy this structure (B). However, the unhinged crystals are now free to be dispersed by mechanical disintegration. Figure C catches the microcrystals in the moment of peeling off the fiber. Properties of the dispersion which forms depend on how effectively they are dislodged.

An entirely new fine structure pattern appears after spray-drying (D). The microcrystals are rehydrogen bonded together, and a spongy, porous, random fine structure partly replaces the highly ordered pattern. Method of drying, initial degree of disintegration, and drying process variables all play a part in developing the inner structure of microcrystalline cellulose flour. At present, only about 20% of the unhinged microcrystals are peeled off the fiber fragments (electron micrographs at 25,000X magnification.)

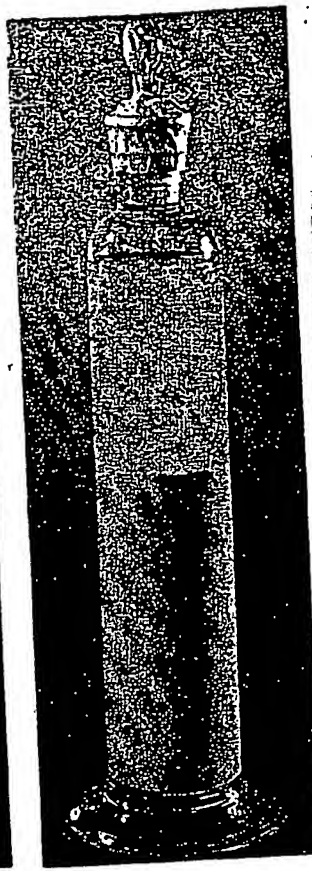
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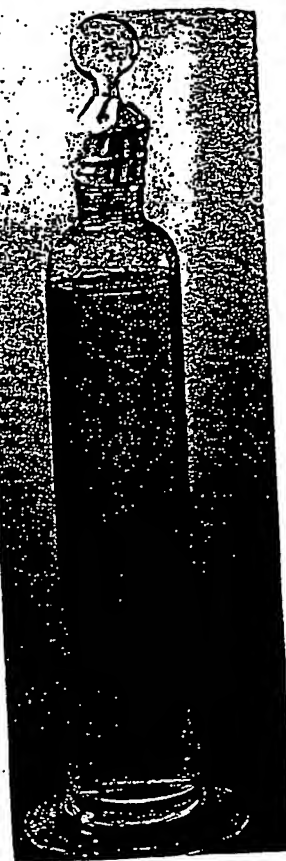
Raw Material



Product



Pulverized fibrous alpha cellulose



Carboxymethylcellulose gum at 2% solids

THESE GELS WERE DISCOVERED WHEN AN EXPERIMENT FAILED

Several years ago we wanted to try out an idea—nucleating viscose spinning solutions with tiny, perfect, unhinged microcrystals of cellulose. We hoped to control the size, perfection, and distribution of the crystalline and amorphous regions in the regenerated cellulose structure. To produce reasonable amounts of these particles, we decided to disintegrate mechanically a concentrated water mixture of D.P. celluloses (left, above) prepared from high strength rayon tire cord. We thought that the sharp blades of a Waring Blendor would sliver off very small fragments of the agglomerated microcrystals in the D.P. cellulose. It was expected that these microcrystalline fragments would settle out of the water.

When D.P. cellulose was placed in water at approximately 5% solids, it settled out rapidly. But when this mixture was treated in a Waring Blendor at high speed for more than 15 minutes, the stable colloidal dispersion shown was obtained. The gel was opaque, snow-white, and had smooth, fatlike spreading properties.

We immediately set out to explore this new avenue, by developing uses for colloidal dispersions of microcrystalline celluloses, known commercially as Avicel (4, 7).

DISPERSIONS OF MICROCRYSTALLINE CELLULOSE ARE UNIQUE

Pulverized fibrous cellulose, which has not been unhinged with acid, does not produce a stable dispersion. Nor do cellulosic gums resemble the new microcrystalline dispersions.

We are dealing with colloidal phenomena related largely to particle size—chemical composition plays a secondary part. The microcrystalline aggregates range in diameter from 150 to 300 A. up to about 5 microns, and are rodlike or lamellar in shape. Unlike the cellulosic gums, the ultimate unit never approaches molecular dimensions (even when diluted).

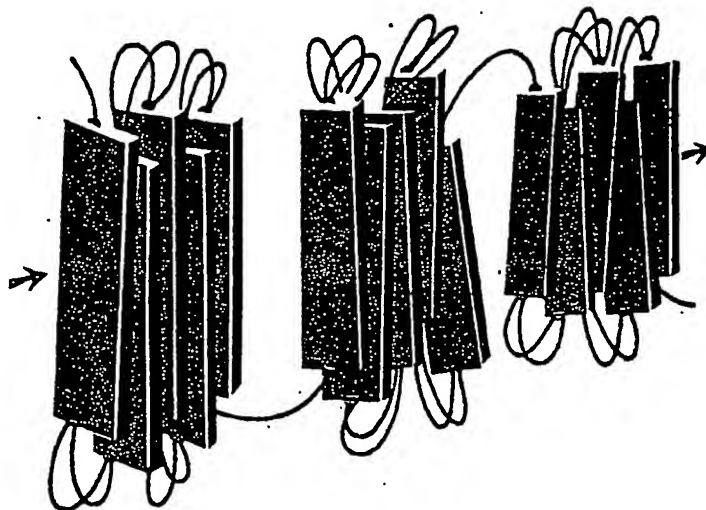
Colloidal microcrystalline dispersions share this size range with bentonite clays and colloidal alumina dispersions—and exhibit many similar properties. It is especially interesting that butter is a stable dispersion in water of fat globules of about the same dimensions. The properties of butter, such as spreadability or sheen, are related to size and size distribution of the fat globules. Some microcrystalline cellulose gels have similarly sized particles and similar functional properties.

Fats and oils in many systems can now be replaced without significant change in appearance, consistency, flow properties, or spreadability.

A Structural Model Was Developed to Explain What Happened in the Blender

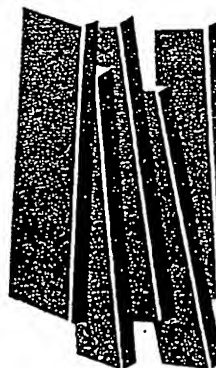
Cellulose molecules form microcrystals, held together by hydrogen bonding. The individual microcrystals are linked by amorphous or disordered areas; one molecule will go through several crystalline areas. Length of the microcrystals and of the hinges is fairly constant for any particular material, depending on its history. The characteristic microfibrils have previously been shown as chains of linked crystals.

We propose this folded structure, with microcrystals packed side-by-side like matchsticks, joined by amorphous hinges. Fiber direction is shown by the arrows

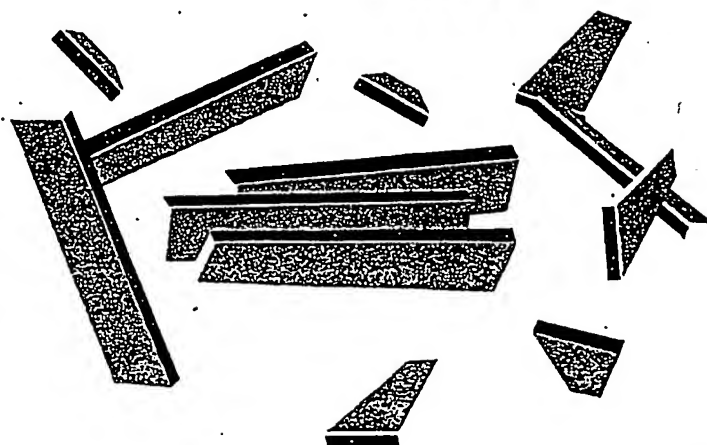


Initially, acid attacks cellulose rapidly. Mild hydrolysis breaks some of the hinges, and recrystallized areas appear. Severe acid hydrolysis breaks all of the molecular hinges and reduces the fiber to isolated crystallites

Reaction rate levels off at this stage. The microcrystals are fairly equal in size, expressed by the "level-off degree of polymerization," or "D.P." Though unhinged, the microcrystals retain their orientation in the fiber



One further step is required to produce colloidal cellulose. Mechanical agitation in a water slurry frees a fraction of the unhinged crystals. With present methods about 20% can be released. Since all of the microcrystals are unhinged, the fraction can be increased by improvement in mechanical techniques only



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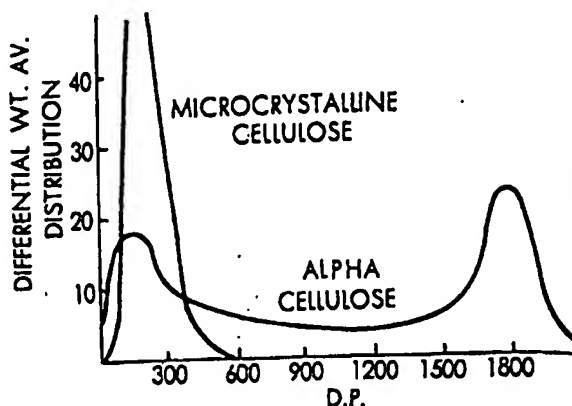
Properties of microcrystalline cellulose can be controlled to fit end use

The unique properties of microcrystalline cellulose stem from its unique particle size and particle size distribution (see table). It is well known that reduction of almost any substance to a narrow colloidal size range can result in drastic changes in functional properties. It is important to note that by using the appropriate mechanical disintegration procedure, particle size and size distribution can be controlled. Functional properties can therefore be controlled over a wide spectrum.

Because the process for making D. P. microcrystalline cellulose breaks the molecular hinges, it results in homogenization of chain length (see figure). Avicel with the narrow molecular weight distribution shown was made from the alpha cellulose sample. (Molecular weight is 163 times the D. P.)

To avoid confusion, these definitions should be kept in mind: level-off D. P. (or D. P.) cellulose is the product resulting from, or equivalent to, the hydrolysis of purified cellulose after 15 minutes in 2.5N HCl at $105 \pm 1^\circ \text{C}$. D. P. varies from about 375 for bleached ramie or hemp to 15 to 25 for extra high strength rayon tire cords. It is a convenient parameter for characterizing the average length of crystalline areas in cellulose.

Microcrystalline cellulose is a mechanically disintegrated D. P. cellulose. It can be prepared from all forms of natural celluloses, alkali celluloses, regenerated celluloses, and even low D. S. cellulose derivatives. Raw material for Avicel microcrystalline cellulose is a special grade of high alpha purified wood cellulose.



Relative Size Range of Microcrystalline Cellulose Particles

Product	Appearance	Range of Diameters
Natural and synthetic gums, starches, and water soluble derivatives	Transparent or translucent aqueous dispersions	5-25 A.
Mechanically disintegrated microcrystalline cellulose	Stable opaque aqueous dispersions	150-50,000 A. (5 μ)
Pulverized fibrous celluloses	Retains fibrous form; two phases in water	40-500 μ , or higher
Microcrystalline cellulose flour	Fine white powder	Few thousand A. to over 10 μ

Previous studies of treatment of cellulose with acids have had few practical or applied objectives. Most of the work has used acid degradation, with moisture regain, and electron microscopy to determine the original molecular architecture (or fine structure) of the fibrous state.

Some milestones are:

- 1875 Girard coined the term, hydrocellulose (13)
- 1925 Hertzog, and Meyer and Mark postulated the crystalline nature of cellulose (15, 25)
- 1937 Staudinger and Sorkin described the dual reaction rates of acid attack (39)
- 1941 Nickerson and coworkers spearheaded the use of acid-feric chloride to study structure (30-32)
- 1943 Davidson demonstrated that molecular weight of cellulose drops rapidly upon initial hydrolysis, then approaches a plateau (17)
- Many others studied reaction rate phenomena and the ratio of crystalline to amorphous regions (3,5,6, 9,10,12,16-20,22-24, 26-29, 33,35-38).

- Midforties Pacsu and coworkers hypothesized a "limit hydrocellulose" which represented a rock-bottom state, resistant to acid degradation (24)
- 1947 Battista and Coppick showed that the so-called limit hydrocellulose was a reflection of crystalline to amorphous ratio, fixed by past history of the cellulose (8)
- 1950 Battista and coworkers advanced the term, level-off degree of polymerization, and proposed a specific definition (above) (3,5)
- and 1956 Average molecular weight and average length of microcrystals have been correlated (5, 23, 28)
- Crystalline nature of cellulose has been substantiated by electron microscopy and x-ray diffraction analyses (3,16,27,35,36)
- 1962 D. A. Zaukelies proposed a new schematic model for the crystalline-amorphous concept in nylons (Chem. Eng. News, p. 48, 49 (April 16, 1962)
- This article Proposes a similar folded arrangement of cellulose molecules hinging the crystalline areas and amorphous regions together (page 23). Presented before the Division of Cellulose, Wood, and Fiber Chemistry, 141st Meeting, ACS, Washington, D.C., March, 1962



NONFIBROUS FLOUR CAN BE A CATALYST CARRIER OR A "FOOD"

Microcrystalline cellulose flour is a very pure form of cellulose, relatively free from both organic and inorganic contaminants. Its x-ray diffraction diagram shows very sharp lines, indicating an unusually high degree of crystallinity.

Density of an individual particle of the flour approaches the absolute density for a single cellulose crystal. Values from 1.539 to 1.545 were determined using a density gradient procedure.

Freeze drying produces a very light powder. Commercial production is by spray drying. Methods such as drum drying or oven drying can be and have been used. The spray-dried product, however, is an unusually fine flour with desirable physical properties.

One of the results of the spongy structure formed on drying is that microcrystalline cellulose will absorb oils and fats. Again, method of drying is important; it can cause a threefold difference in oil saturation value. Commercial product has intermediate absorption characteristics. Examples of its capacity are given opposite.

Foods are not the only application of this property. Catalysts and reactive chemicals can be applied, carried on a colloidal solid. Water-soluble dyes can be transported into oils and fatlike material without blooming. It can be an inert and edible substrate for vitamins, antibiotics, and essential oils.

Peanut butter with microcrystalline cellulose flour can be sprinkled from a shaker. A convenience in the home, this may lead to economies in the food factories of tomorrow.

The flour will convert many materials to free-flowing form when used in the amounts below.

Ingredient	Commercial Microcrystalline Cellulose, %	Ingredient	Commercial Microcrystalline Cellulose, %
Peanut butter	23.0	Maple syrup	44.0
Swiss cheese	13.8	Butter	44.8
Cheddar cheese	20.0	Lemon oil	50.0
Blue cheese	36.0	Orange oil	50.0
Plastic coconut	20.6	Corn oil	39.0
Molasses	44.0	Hydrogenated fat	39.0
Honey	44.0	Milk chocolate (melted)	32.4

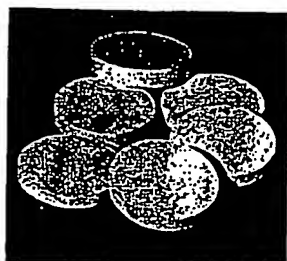
Bulk Density of the Flour Depends on Method of Drying

	Lb./Cu. Ft.
Freeze dried	9.8
2-Propanol-washed	13.3
Methanol-washed	14.0
Spray-dried (commercial production)	16.0-20.0

Commercial Microcrystalline Cellulose Flour	
Molecular weight	30,000-50,000
Moisture, %	< 5
Organic solvent extractables, %	< 0.03
Ash, %	< 0.05
Calcium, p.p.m.	< 40
Chlorides, p.p.m.	< 50
Iron, p.p.m.	< 10
Copper, p.p.m.	< 4
Solubility	
Water	Insoluble; dispersible
Dilute alkali	Partially soluble; swells
Dilute acid	Insoluble; resistant
Organic solvents	Insoluble; inert
Oils	Insoluble; inert



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COMPRESSED FLOUR— FOR TABLETS OR FLAME- RESISTANT BOARD

A structural material so compact that it cannot be penetrated by an ordinary nail results when the flour is compressed at room temperature and 15,000 p.s.i. It has a surprising degree of resistance to an oxyacetylene torch (see table, below).

Extremely strong tablets can be formed of this material in normal tableting equipment. Catalysts, essential oils, or pharmaceuticals could still be absorbed on the tremendous internal surface of these tablets.

Compressed tablets break up immediately in liquid water, as the hydrogen bonding is destroyed. Freedom from amorphous cellulose makes them relatively insensitive to water vapor. The tablets would therefore retain their properties in a humid atmosphere, but instantly release their active components on contacting water. Water resistance can be built in by formulating with a protective resin such as an urea formaldehyde.

Electrical properties of the compressed powder structures are very similar to those of vulcanized fiber. With protective resin treatment, these properties can be maintained at high relative humidities.

Moisture Pickup Is Lower Than That of Any Other Form of Cellulose

R.H., % (77° F.)	H ₂ O, % (After 48 Hr.)
15	2.5
45	5.7
58	6.0
81	6.2

*Compressed Flour Form of Microcrystalline D.P. Cellulose
(Without resin treatment)*

Density, lb./cu. ft.	86-98
Specific gravity	1.26-1.34
Thermal conductivity, B.t.u./in. sq. ft. ° F. hr.	1.75
Specific heat, B.t.u./lb. ° F.	0.4
Power factor, % (58% R.H., 72° F.)	2.88
Power factor of vulcanized fiber (electrical grade), %	6.0
Dielectric constant (58% R.H., 72° F.)	5.6
Impact strength, ft.-lb./in. of notch	~ 1



STRUCTURAL CELLULOSE— FOR HEAT SHIELDS OR "MARBLE" SLABS

An ivory-like material is produced by drying an aqueous colloidal gel of D.P. microcrystalline cellulose. Structural forms from these dried gels are generally superior in physical properties to the compressed flour forms. They are more resistant to moisture, although they will swell when in prolonged contact with liquid water (for several days). They are harder, stronger, and denser. An important difference is much better impact strength.

The electrical properties of the dried gel are almost identical with the pressed structure and with electrical grade vulcanized fiber. Method of manufacture of the new material involves only room temperature drying. Desired shapes can be molded during production. For

*Cellulose Structures Have Much Greater Heat Resistance Than
Asbestos Materials*

Product	Bulk Density, Lb./ Cu. Ft.	Heat Con- ductance, B.t.u./Sq. Ft. ° F. Hr.	Specific Heat, B.t.u./ Lb. ° F.	Time under Oxy- acetylene Torch, Sec.
Compressed flour- 1/2 in. disk	86	1.80	0.4	15 (not through)
Transite, 1/2 in.	112	4.50		7 (through; melts)
Marinite, 1/2 in.	75-80			7 (through; melts)
Dried gel struc- ture, 1/2 in. block*	~95			70 (crater depth, ~ 1/2 in.)
1/2 in. Steel				5 (Through; melts)

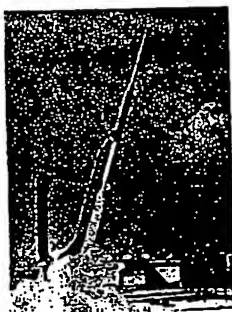
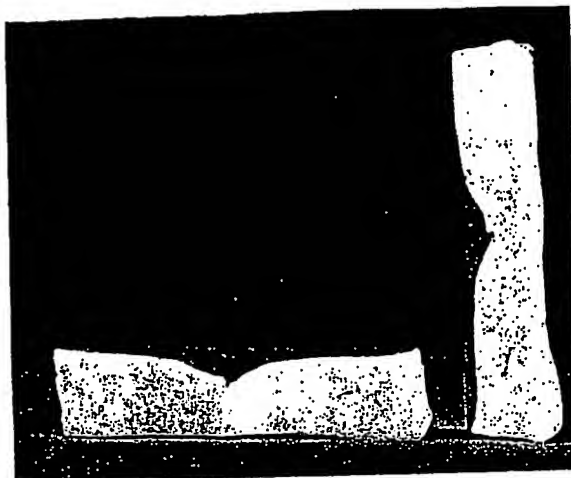
* 6500° F. b Dried from 15% microcrystalline cellulose gel.

electrical use, a material similar in electrical properties to vulcanized fiber, with some superior physical properties, can be manufactured and fabricated much more easily.

The dried gels will withstand an oxyacetylene torch three to four times longer than the compressed flour. The erosion process is most interesting—ablation involves only surface carbonization with an attendant slow erosion.

Heat conductivity is less than that of the compressed flour structure.

The interior of this block (a dried gel structure) is completely unchanged by heat. It was subjected to an oxyacetylene torch for 30 seconds, then sawed in half. The sample could be handled almost immediately after the flame was removed, showing the very low thermal conductivity of the material



DERIVATIVES OF CELLULOSE CAN BE COLLOIDAL TOO

Reaction of the microcrystalline cellulose proceeds with particular ease and speed. Derivatives can be formed which are also colloidal. These are entirely new materials with very different properties and potential applications.

At high degrees of substitution (D.S.) derivatives of microcrystalline cellulose are substantially the same material as produced from conventional cellulose. At low D.S. where the colloidal nature is maintained with surface substitution, the derivatives from colloidal dispersions. Dispersions of at least 20% solids in water can be produced. These may have the appearance of greases, ointments, or lotions, depending on the materials present.

An example of a new type of derivative, microcrystalline carboxymethylcellulose at low D.S. is shown. In dispersion at about 20% solids, this is a partly opaque nongreasy spreadable ointment with a consistency which suggests use as a suntan lotion. It does not remotely resemble the stiff conventional gel of CMC shown on page 22. The photomicrograph shows the reasons for this difference.

Other derivatives can be prepared. Methyl-, ethyl-, and hydroxypropylcelluloses with unusual properties have been studied. Nitrated D.P. cellulose derivative has particularly important potential applications in solid rocket propellants; it can be readily made into a particulate form with particles in the 1-to 3-micron range. Properties of all of these materials can be con-



A low D.S. carboxymethyl derivative of microcrystalline cellulose. Instead of a solution of molecular dimensions, the freed microcrystals remain substantially unchanged in size. Microfibrils of unhinged but unfreed microcrystals also are left intact

trolled over a wide range by varying degree of substitution, the heterogeneity of this substitution, and the nature of the topochemically substituted group.

Microcrystalline D.P. celluloses in flour form exhibit an unusual affinity for hydrophobic reactants, including catalysts, which is believed to be related to the sub-microscopic porosity of the particles. Distribution of such active chemicals over such large surface areas of cellulose proffers new advantages in preparing cellulose derivatives.

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COLLOIDAL GELS— FOR FOOD PRODUCTS OR COATINGS

Redispersion of the colloidal flour in water gives white, opaque gels or creams with functional properties which suggest many applications in a variety of industries. Some of these are:

—Gels are thixotropic and are stable over a period of years except at extreme dilution. A moldable gel is formed at about 20% solids. Dilution to 10% solids produces a pourable cream.

—The colloidal particles have an electronegative charge. —Colloidal dispersions can be used to form extremely adherent films and coatings on glass (7). It is possible that such a coating on glass fiber would provide a cellulosic surface, adapting the fiber to normal textile weaving equipment.

—A similar extremely thin adherent film can be deposited on aluminum. Electrical capacitors could be built up, using films a few microcrystals thick.

—Gels and dispersions possess unusual compatibility with emulsions of oils and fats, as well as with sugar.

—A 15% dispersion of microcrystalline cellulose may be sterilized in a closed container for at least one hour at 240° F. without any breakdown of the stability of the gel. A viscosity increase is usually observed.

—The addition of emulsified fats or oils as well as the addition of significant amounts of sugar to a 15% colloidal dispersion of microcrystalline cellulose permits these mixtures to be deep-frozen or thawed repeatedly without significant breakdown of the gel structure and attendant syneresis. Without the presence of other components, quick freezing leads to a breakdown of the suspensions upon thawing.

—At high dilutions, they do not disperse to particles of molecular dimensions: the smallest dispersed particles are the unit microcrystals which consist of tightly packed bundles of several hundred cellulose molecules.

Viscosity of Dispersions. The solids concentration, at the time of the mechanical disintegration step, is a major variable in the development of the viscosity and the thixotropic properties of gels as well as stable colloidal dispersions with microcrystalline D.P. celluloses.

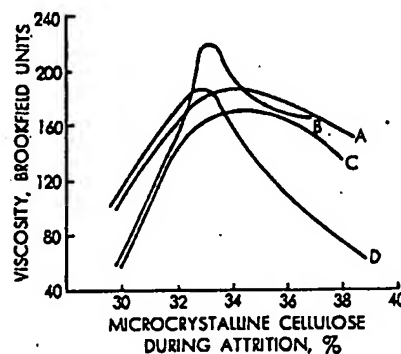
The optimum solids content to produce maximum dispersion will vary with each type of equipment used for the mechanical disintegration step. For example, 40 to 50% solids for a roll mill, 34 to 36% solids for a Hobart mixer with solid paddle, 10 to 15% for a Waring Blender or an Osterizer, and 10 to 20% for piston-type homogenizers.

As shown in the graph, viscosity of a gel depends on attrition equipment, past history of the cellulose, and concentration during attrition.

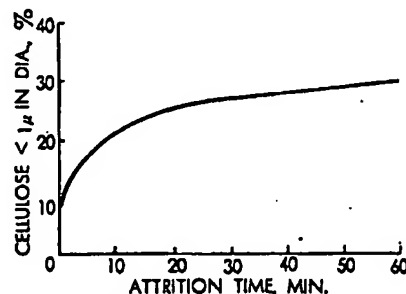
Effect of PH on Viscosity of 5% Colloidal Dispersion

pH ^a	Av. Apparent Viscosity ^b
7	8.8
8	93.4
9	118.2
10	148.8
11	61.1

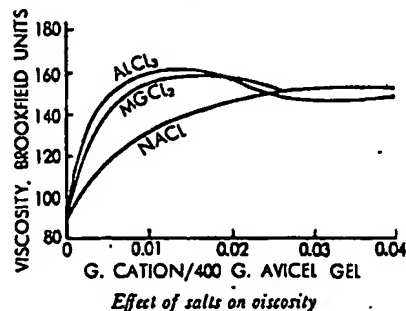
By adding NH₄OH. Ostwald viscometer.



The attrition step must be performed in a rather critical concentration range. The dry flour was mixed with water under the conditions shown, and viscosities were measured after dilution to 15%. A, commercial spray-dried, Hobart, 20 min.; B, never dried, Hobart, 20 min.; C, lab. spray-dried, Hobart, 20 min.; D, commercial spray-dried, Mixer, 10 min.



Attrition develops particles of colloidal size



Effect of salts on viscosity

Effect of Disintegration Time. Mechanical disintegration with time develops varying amounts of true colloidal size particle aggregates that are less than 1 micron in diameter. These are the particles freed from the fiber. These particles remain in permanent suspension. It is the extent to which they are developed which controls the stability and many of the functional properties of the resulting colloidal suspensions or gels.

Microcrystalline cellulose dispersions or gels retain their colloidal stability as long as the mechanical disintegration produces a sufficient amount of the hydrated submicron particles to support a continuous gel network. Such physical properties of the gels as viscosity, stiffness, and stability are related to the particle size distribution of the gel. At the same solids content, gels prepared by means of a Waring Blendor, for example, have properties that are different from gels prepared by a laboratory Hobart mixer at higher solids content with subsequent dilution. Microscopic examination of such gels reveals major differences in the size and distribution of the visible particles.

Effect of pH. Data on one of the original colloidal dispersions (prepared using a Waring Blendor) show that the apparent viscosity of a 5% colloidal dispersion of

D.P. cellulose reaches a maximum at pH of about 9 to 10.

Effect of Salts. As might be expected, salts have varying influences on the apparent viscosity of colloidal dispersions from D.P. celluloses. Interestingly enough, if salts are present in the aqueous mixture at the time of the mechanical disintegration, the subsequent viscosity development is decreased. On the other hand, addition of salts, once the stable colloidal gel is produced, usually increases the apparent viscosity.

Producing the Gel. Dilution of stable colloidal dispersions of microcrystalline cellulose at high solids concentrations should be carried out gradually to reduce localized over-dilution and a tendency for the agglomeration of relatively large particles. When mechanical disintegration of microcrystalline cellulose at high solids contents is extended for a long time, or when localized over-dilution occurs, reagglomeration of some of the particles may take place in the form of spherical masses. Such reagglomerates, because they behave similar to a swollen mass of gel, are difficult to redisperse. They are receptive to breakdown by commercial homogenization equipment, however. We refer to them as rosettes because of their tendency to form rose-shaped particles.

MICROCRYSTALLINE CELLULOSE CAN BE USED SAFELY IN FOODS AND COSMETICS

X-ray diffraction patterns of D.P. celluloses establish microcrystalline cellulose as the purest form of cellulose now available. Microcrystalline cellulose is generally recognized as safe by experts. A long history of cellulose as a vital ingredient in a host of natural foods is well recognized, and has been clinically substantiated over many years. Celery, cabbage, cereals, and many other plant and vegetable foods have varying amounts of cellulose in them. It is therefore not an additive and, as such, is not subject to the clearance provisions of the Food Additives Amendment of 1958.

Research investigations with Avicel in animals and humans were planned at an early stage in the initial development. Several phases of these programs have been completed and others are still in progress. As part of this research program a human clinical investigation has been completed (14). No adverse effects were found. Both microcrystalline and natural plant cellulose pass through the human body without evidence of breakdown.

BACKGROUND LITERATURE

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**Fig.1 Measurement apparatus for
dynamic viscoelasticity of liquid sample**

ARES (Advanced Rheometric Expansion System) 100FTRN

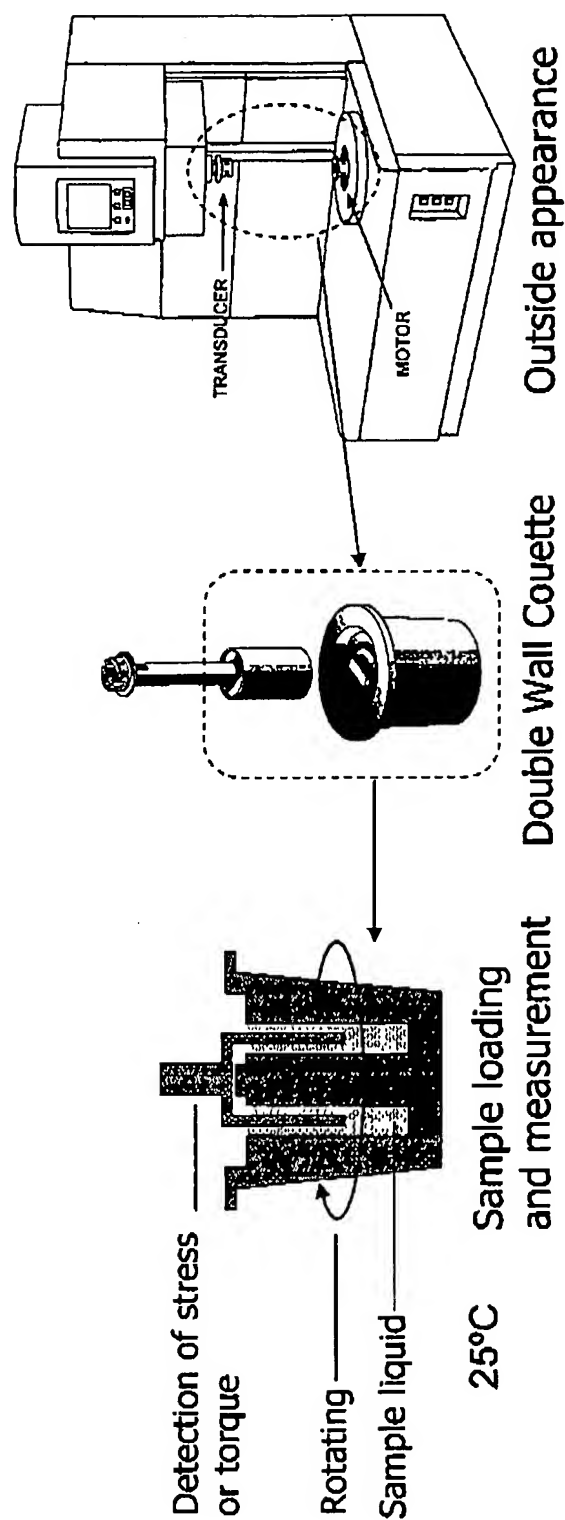
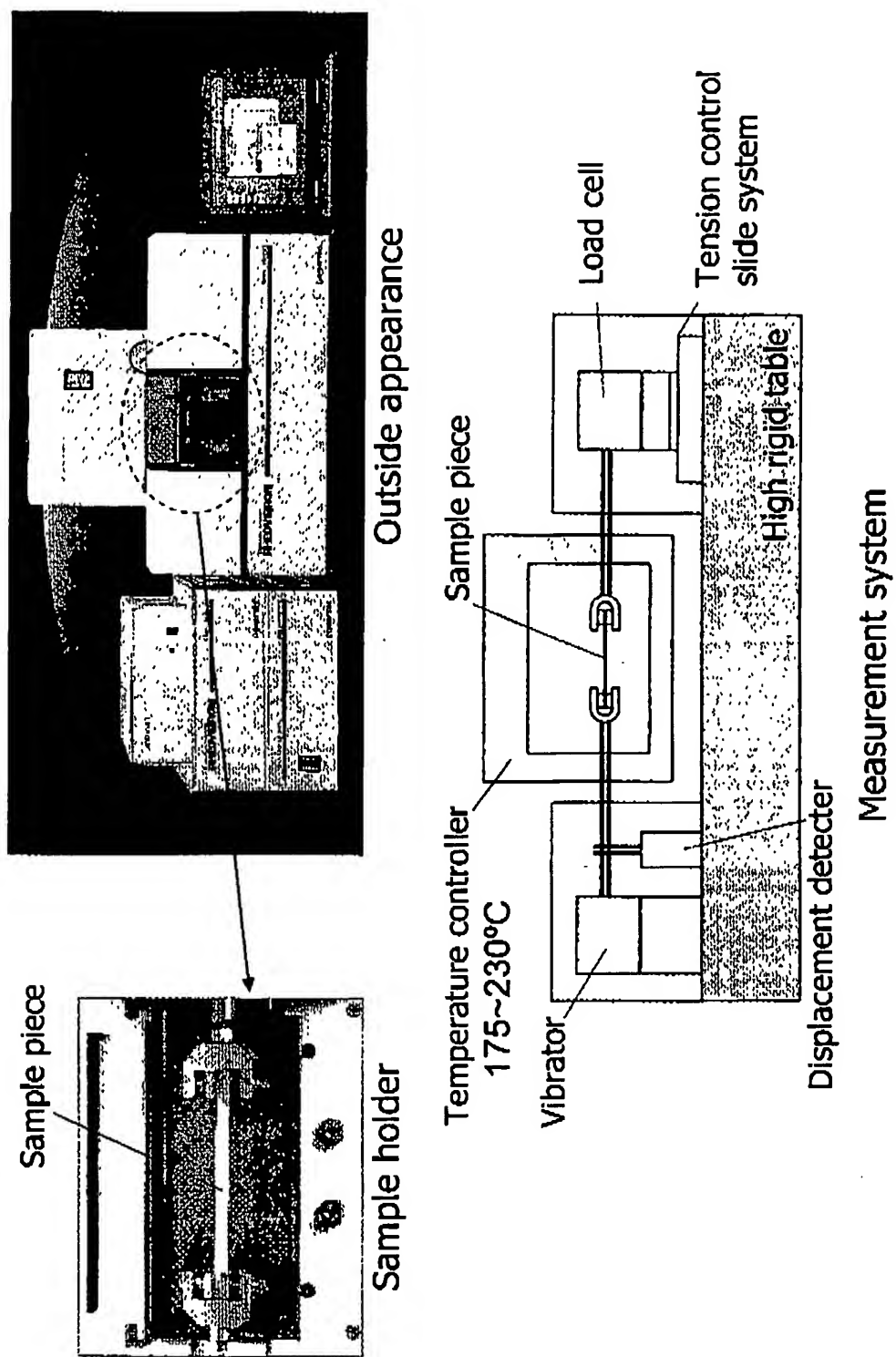


Fig. 2 Measurement apparatus for dynamic viscoelasticity of solid sample

RHEOVIBRON



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denoted by a significant increase in loss in weight due to decomposition.

To obviate the difficulties in determining the critical temperatures from curves which do not show a sharp inflection, an equation is suggested which more closely defines the separate effects of rate and extent of decomposition, temperature, duration of test, and resin content of the material.

Classification of the materials studied in accordance with their critical thermal instability temperatures and with the per cent resin losses at this temperature has been tentatively made pending further study and evaluation in service.

ACKNOWLEDGMENT

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Hydrolysis and Crystallization of Cellulose

3394

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A comprehensive study has been made of the effect of time on the weight loss and degree of polymerization of ten representative samples of cellulose using both mild (5.0 *N* hydrochloric acid at 5°, 18°, and 40° C.) and drastic (2.5 *N* and 5.0 *N* hydrochloric acid at boil) conditions of hydrolysis. The samples were purified cotton, bleached cotton linters, cotton linters pulp, wood pulp, textile rayon, tire yarn, Fortisan, Fiber G, and two experimental rayons. The per cent crystallinity as measured by acid hydrolysis (based on weight of residue) and the leveling-off degree of polymerization are shown to be dependent on whether mild, drastic, or mild plus drastic conditions of

hydrolysis are employed. The use of 2.5 *N* hydrochloric acid at 105° C. for 15 minutes is recommended as optimum conditions for measuring weight loss or relative crystallinities and leveling-off degrees of polymerization in conjunction with apparatus described. On the basis of weight loss and degree of polymerization data, mechanisms are proposed to account for the crystallization of cellulose chains simultaneously with chain splitting under conditions of mild and drastic hydrolysis, respectively. The effect of crystallization on hydrolysis was found to be more pronounced for regenerated celluloses than for native celluloses.

ONLY in relatively recent years has the heterogeneous hydrolysis of regenerated celluloses received much attention. A great deal of the early work, such as that by Brissaud (6), Birtwell, Clibbens, and Geake (3), and Worner and Mease (25), was concerned primarily with the action of acids on cottons, with the object of determining variations in the physical properties of the cotton fibers upon acid degradation.

The use of acid hydrolysis as a chemical method for characterizing the molecular chain architecture of cellulose fibers was pioneered through a series of papers by Nickerson (16-18) and later by Nickerson and Habre (20-22). The Nickerson approach was to subject a sample of cellulose to a boiling solution of 2.45 *N* hydrochloric acid and 0.6 *M* ferric chloride.

Under this drastic hydrolyzing treatment, cellulose chains become split rapidly at the available 1,4 glycosidic bonds, producing short-chain cellulose and ultimately glucose. In the presence of ferric chloride, the glucose formed is catalytically oxidized to carbon dioxide and water. By following the rate of carbon dioxide evolution with time of hydrolysis, it was believed that the "accessibility" of the original fine structure could be characterized.

Two rather distinct reaction rates were observed, and they were explained on the basis of a two-phase fine structure—one part amorphous and readily attacked by the acid, the other crystalline and only very slowly attacked by the acid. It was proposed at the time that the amorphous material present in the original sample was gradually reduced to acid-soluble end products, leaving behind the acid-resistant crystalline component as a residue. A quantitative evaluation of the amount of crystalline and amorphous cellulose was attempted on this basis. Paralleling the original Nickerson papers, Davidson (7)

in 1943 published details of an extensive study covering the prolonged action of acids on cotton cellulose. Many of his results and conclusions were the same as those of Nickerson. He found a sharp drop in moisture regain on hydrolysis, even when a very small loss in weight occurred. The drop in moisture regain was explained on the basis of the removal of amorphous or water-sensitive material. Davidson reported leveling-off degrees of polymerization for cotton and mercerized cotton, the value for cotton being higher than for mercerized cotton. He claimed no significant difference between the x-ray diagram of powdery hydrocelluloses and the original cotton, no matter how he prepared them. A study of the heterogeneous decomposition of cellulose by acids was conducted at about the same time by Eisenbut and Schwartz (8).

Conrad and Scroggie (9) proposed important improvements for the Nickerson carbon dioxide-evolution technique. Lovell and Goldschmid (14) chose to estimate the glucose formed on drastic hydrolysis by measuring the actual loss in weight of the sample instead of the rate of carbon dioxide evolution. Philipp, Nelson, and Züfle (23) dropped the use of the ferric chloride oxidation catalyst of the Nickerson reagent, and proposed using 6 *N* hydrochloric acid at the boil for hydrolyzing native cellulose structures and 4 *N* hydrochloric acid at the boil for hydrolyzing regenerated structures. Philipp *et al.* measured the weight of the hydrocellulose residues remaining after hydrolysis, correcting for humic substances which were formed under the conditions employed.

More recently, Nelson and Conrad (15) suggested improvements in the original Philipp *et al.* procedure, whereby a more satisfactory correction for humic substance formation is possible.

The use of much milder conditions of hydrolysis (5 *N* hydro-

chloric acid at 18° C.) for the chemical characterization of cellulose fine structure was proposed by Battista and Coppick (8), who demonstrated that on prolonged mild acid hydrolysis the basic degree of polymerization of most native structures tended to level off at much higher values (325 to 275) than was the case for regenerated structures (40 to 80); mercerized cellulose structures tended to level off in a basic degree of polymerization range somewhere between (75 to 125).

Nickerson and Habrie (28) investigated less severe conditions of hydrolysis (2.5 N sulfuric acid at the boil) than were used with the original Nickerson reagent (boiling 2.45 N hydrochloric acid-0.6 M zinc chloride solution) to follow more accurately the rapid initial phase of the hydrolysis process. They also pointed out differences in the so-called "limiting D. P." values for native, mercerized, and regenerated structures, respectively, and suggested that the leveling-off degree of polymerization on drastic hydrolysis might correspond to the average crystallite length. Roseveare, Waller, and Wilson (24) suggested that the limiting degree of polymerization on hydrolysis of regenerated cellulose might correspond to the average length of a chain passing through one crystalline and one disordered region.

On the basis of x-ray data, Ingersoll (12) proposed that relatively mild hydrolysis might cause the crystallization of cellulose chains simultaneously with chain splitting. Howsman (11) published moisture regain, weight loss, and x-ray data, showing that the drop in moisture regain and the sharpening of the x-ray diagram could not be explained by the very small loss in weight, due presumably to the removal of amorphous cellulose. In his paper, Howsman compared physical and chemical methods for characterizing cellulose fine structure and proposed that hydrolytic methods give high values for the crystallinity of cellulose because additional crystallization of the chains occurs on hydrolysis.

Brenner, Frlotte, and Mark (4) came to a similar conclusion on the basis of specific volume and density measurements made on hydrolyzed cellulose. More recently, using improved x-ray techniques to follow changes in crystallinity on hydrolysis, Hermans and Weidinger (10) obtained data to confirm further the belief that with regenerated cellulose, at least, crystallization of the cellulose occurs simultaneously with chain splitting on acid hydrolysis.

In this investigation, the effects of such variables as time, temperature, and acid concentration on the hydrolysis of the fine structures of both native and regenerated celluloses have been studied. Comprehensive data on weight loss and degree of polymerization have been obtained for a wide variety of celluloses which were subjected systematically to hydrolyses under mild and drastic hydrolysing conditions.

Combined data on weight loss and degree of polymerization demonstrate that the mechanism of the crystallization which accompanies hydrolysis is controlled by two interdependent processes—hydrolysis and crystallization. It is suggested on the basis of the data that conditions of mild hydrolysis, during which 1,4 glycosidic bonds are split at a relatively slow rate, favor the formation of longer, less acid-soluble crystallized material. Drastic conditions of hydrolysis, on the other hand, promote the formation of very short, more acid-soluble crystalline material.

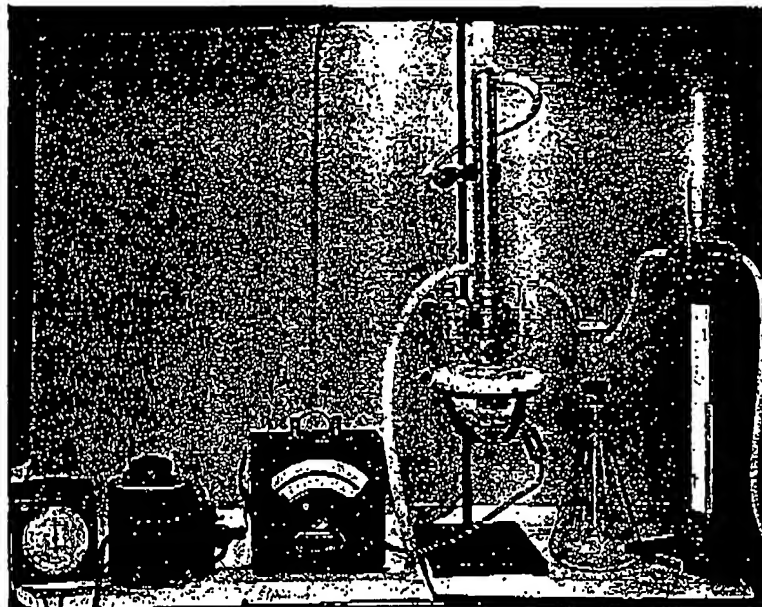


Figure 1. Apparatus for Measuring Per Cent Crystalline Residue
Standard drastic conditions, 15 minutes in 2.50 N hydrochloric acid at 185° C.

SAMPLES STUDIED

Ten samples of purified celluloses, representative of both native and regenerated cellulose fine structures, were selected for this study:

No.	Sample	Original Basic D. P.
I	Purified cotton	3200
II	Bleached linters	1800
III	Linter pulp	850
IV	Wood pulp	1050
V	Avisco tire yarn (high tenacity, highly oriented regenerated cellulose yarn)	490
VI	Avisco textile yarn (regenerated cellulose rayon, normal tenacity and orientation)	470
VII	Experimental rayon (HST)	440
VIII	Experimental rayon (LST)	350
IX	Fortisan	450
X	Fiber G	550

EXPERIMENTAL PROCEDURES

MEASUREMENT OF DEGREE OF POLYMERIZATION. The method used for measuring viscosities in cuprammonium solvent was essentially that described by the author (1).

Viscosities were determined on solutions having a concentration of 0.50% cellulose. The viscosities were converted to basic degrees of polymerization where the basic D. P. = $2160 [\log (\eta + 1) - 0.267]$ for celluloses having a degree of polymerization greater than 300 (1). In the case of 0.5% solutions of cellulose having a basic degree of polymerization less than 300, it has been shown (1) that η_{sp}/c is equivalent to $[\eta]$, where $[\eta]$ is the value of the intrinsic viscosity at infinite dilution. For hydrocelluloses having a degree of polymerization less than 300, therefore, the Kraemer (13) constant applies and D. P. = $260 \times \eta_{sp}/c$, where c equals concentration, grams per 100 ml. of solution, and is 0.5% or less.

MILD DEGRADATION PROCEDURE. The ten samples were hydrolyzed in 5 N hydrochloric acid at 5°, 18°, and 40° C., respectively, for varying lengths of time.

All samples were subjected to a standard nondegradative extraction and scouring procedure to free them of waxes and finishes. With the exception of the two rayon-grade pulps, which were fluffed in a Waring Blender to loosen the fibers prior to hydrolysis, the fibers were cut to approximately 0.25-inch lengths

TABLE I. AVERAGE BASIC DEGREE OF POLYMERIZATION IN 5 N HYDROCHLORIC ACID

	Raw Cotton				Bleached Cotton Linters			
	5° C.	18° C.	40° C.	Boil	5° C.	18° C.	40° C.	Boil
Controls	3200	3200	3200	3200	1900	1900	1900	1900
15 min.	3190	1880	1131	240	882	774	651	280
30 min.	1780	1590	918	..	824	737	680	..
1 hour	1630	1520	723	..	831	707	535	..
2 hours	1630	1440	548	..	823	680	439	..
4 hours	1590	1249	484	..	795	630	385	..
6 hours	1560	1150	450	..	787	610	360	..
8 hours	1483	1085	40	..	784	675	370	..
24 hours	1060	733	705	479
Cotton Linters Pulp								
Controls	880	880	880	880	1030	1030	1030	1030
15 min.	871	771	574	280	1016	948	742	297
30 min.	865	743	495	..	1002	940	668	..
1 hour	844	735	410	..	99	924	686	..
2 hours	808	700	352	..	870	848	514	..
4 hours	764	670	330	..	940	743	44	..
6 hours	750	652	302	..	930	718	398	..
8 hours	746	605	293	..	912	690	353	..
24 hours	633	476	858	475
Fiber G								
Controls	660	660	660	550	450	450	450	450
15 min.	495	487	402	60	446	438	370	65
30 min.	460	484	340	..	425	428	353	..
1 hour	473	470	285	..	429	395	300	..
2 hours	450	440	240	..	437	368	265	..
4 hours	425	413	165	..	398	337	190	..
6 hours	423	370	170	..	402	308	181	..
8 hours	415	364	143	..	400	297	152	..
24 hours	404	240	372	276
Tire Yarn								
Controls	470	470	470	47	490	490	490	490
15 min.	460	420	371	45	482	455	377	55
30 min.	461	401	310	..	490	429	310	..
1 hour	458	378	370	..	478	409	260	..
2 hours	451	350	311	..	476	390	185	..
4 hours	435	337	160	..	465	373	135	..
6 hours	409	323	105	..	455	355	120	..
8 hours	400	308	82	..	440	335	90	..
24 hours	390	200	375	238
High Salt Test Yarn								
Controls	440	440	440	440	350	350	350	350
15 min.	389	402	358	40	318	298	265	65
30 min.	379	383	303	..	309	285	225	..
1 hour	379	356	259	..	303	277	190	..
2 hours	373	347	195	..	289	257	164	..
4 hours	363	342	180	..	280	255	120	..
6 hours	360	335	115	..	281	240	115	..
8 hours	354	323	90	..	277	231	112	..
24 hours	350	325	274	213
Low Salt Test Yarn								
Controls	440	440	440	440	350	350	350	350
15 min.	389	402	358	40	318	298	265	65
30 min.	379	383	303	..	309	285	225	..
1 hour	379	356	259	..	303	277	190	..
2 hours	373	347	195	..	289	257	164	..
4 hours	363	342	180	..	280	255	120	..
6 hours	360	335	115	..	281	240	115	..
8 hours	354	323	90	..	277	231	112	..
24 hours	350	325	274	213

with sharp scissors to secure uniform samples. All samples were conditioned at 58% relative humidity and 74° F.

Two (2,000) gram portions (oven-dry) were weighed out and referred to 250-ml. sample bottles, and 200-ml. aliquots of 5.0 N hydrochloric acid, taken from stock bottles maintained at the respective temperatures, were added to each sample. The samples were dispersed uniformly in the large excess of acid, and the bottles were stoppered and stored for varying times in accordance with a prearranged schedule. At the end of each specified hydrolyzing period, the samples were transferred immediately to fritted-glass filters and washed acid-free with distilled water, 5% ammonium hydroxide, and more distilled water. The residues were then dried in a vacuum oven (30 inches of mercury) for 5 hours at 105° C., prior to conditioning them to equilibrium at 58% relative humidity, and measuring their basic degrees of polymerization. Where weight losses were measured, the residues were weighed out in the oven-dry state. Repeated tests have shown that the foregoing drying conditions do not degrade the hydrocellulose residues beyond the experimental accuracy of the degree of polymerization measurement. It is important, however, to make absolutely certain that the hydrocelluloses are acid-free before drying, and dilute ammonium hydroxide washings will ensure this.

DRASTIC DEGRADATION PROCEDURE. The apparatus used for hydrolyzing the samples in boiling hydrochloric acid is illustrated in Figure 1.

The hydrochloric acid solution was heated by means of a Glas-Col mantle connected in series with a powerstat. An ammeter was used to regulate a constant and reproducible supply of heat to the mantle. A steady stream of dry nitrogen gas

(100 cc. per minute) was admitted through one opening of the three-necked flask for the purpose of keeping the temperature of the acid uniform, eliminating bumping, and excluding oxygen from the hydrolyzing medium. The temperature of the boiling 2.50 N hydrochloric acid was kept at 105° ± 0.50° C.

Two (2,000) gram portions (oven-dry basis) of a sample of known moisture content were weighed out and added to 300 ml. of 5.0 N or 2.50 N hydrochloric acid solution (as indicated), previously brought to the boil. Samples were soaked with 15-ml. aliquots of the respective hydrochloric acid solution to facilitate their transfer.

The sample of cellulose was left in the boiling hydrochloric acid for precisely the times specified. The apparatus was dismantled at the end of the hydrolysis treatment, and the contents of the flask were transferred to a tared fritted-glass filter of D porosity. The time required to dismantle the apparatus and transfer the hydrocellulose residue to the filter was never longer than 60 seconds.

The sample was then washed repeatedly with distilled water, dilute ammonium hydroxide (5%), and more distilled water until acid-free, after which it was dried in a vacuum oven to constant weight at 105° C. All residues of samples hydrolyzed up to 30 minutes in 2.50 N hydrochloric acid were snow-white in appearance after washing and drying as above.

RESULTS

Changes in basic degree of polymerization with time of hydrolysis by 5.0 N hydrochloric acid at 5°, 18°, and 40° C., and at the boil, respectively, are tabulated in Table I and plotted for representative samples (cotton linters pulp and viscose tire yarn) in Figures 2 and 3. As these data show, the basic degree of polymerization tends to level off at a higher value the lower the temperature of hydrolysis.

It was found that the hydrolysis of cellulose by 5.0 N hydrochloric acid at the boil for periods of time longer than 15 minutes gave rise to the formation of humic substances. For the purpose

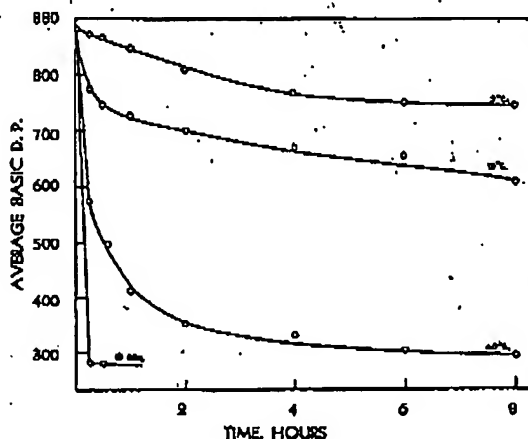


Figure 2. Hydrolysis of Native Cellulose (Cotton Linters Pulp)

5.0 N hydrochloric acid with increasing temperature

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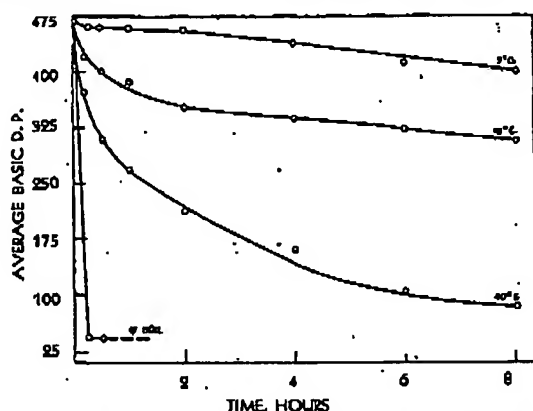


Figure 3. Hydrolysis of Regenerated Cellulose (Viscose Tire Yarn)
5.0 *N* hydrochloric acid with increasing temperature

of weight loss studies, therefore, hydrolyzing conditions under which the formation of humic degradation products is prevented or maintained at a negligible minimum were selected. Boiling 2.50 *N* hydrochloric acid for 15 minutes was found to meet these requirements. The criterion on which the foregoing assumption was based was the visual absence of any insoluble, dark-colored matter which is characteristic of the presence of very small traces of humic substances, even when hydrolyzing times up to 30 minutes were used.

Quantitative data showing the loss in weight with time of hydrolysis in boiling 2.50 *N* hydrochloric acid for a native cellulose (purified cotton) and a regenerated cellulose (viscose tire yarn), respectively, are given in Table II and plotted in Figure 4. One might expect that the slopes of the straight-line portions of the curves of weight loss versus time would be related in some way with the accessible surface area of the crystalline hydrocellulose aggregates, once the leveling-off degree of polymerization is reached. Indeed, each sample gives a slope characteristic of it, and work is in progress with a view to estimating the surface areas of crystalline hydrocellulose particles by this means.

TABLE II. QUANTITATIVE WEIGHT LOSS DATA WITH TIME OF HYDROLYSIS

Hydrolysis Time, Min.	Purified Cotton		Tire Yarn	
	% Hydrocellulose residue	Basic D. P.	% Hydrocellulose residue	Basic D. P.
Control		3200		470
6	92.01	257	78.5	52
10	91.43	244	72.1	49
15	91.03	242	70.9	48
20	90.05	233	61.5	40
30	89.79	230	53.6	40

CALCULATION OF RELATIVE RATE CONSTANTS

Using the degree of polymerization-time data shown in Table I (expressed as $1/[\eta]$ vs. t) relative hydrolysis rate constants may be calculated by adapting the equation of Ekenstam (9). The Ekenstam equation, meant to apply to the homogeneous hydrolysis of 1,4 glycosidic bonds, is as follows:

$$K = \frac{1}{t} \ln \left\{ \frac{1 - \frac{m}{M}}{1 - \frac{m}{M_0}} \right\}$$

where t = time hydrolysis in minutes, M = initial molecular weight, M_t = molecular weight after time t , and m = final molecular weight.

However, when M and M_t are large with respect to m , the above equation simplifies to:

$$K = \frac{m}{t} \left\{ \frac{M - M_t}{M \times M_t} \right\} = \frac{1}{t} \left\{ \frac{DP_0 - DP_t}{DP_0 \times DP_t} \right\}$$

where DP_0 = original degree of polymerization, and DP_t = degree of polymerization after time t .

By calculating relative hydrolysis time constants, K_r , with the above simplified equation, for samples having similar original and leveling-off degrees of polymerization at two different temperatures, relative energies of activation, E_r , may be calculated by adapting the classical Arrhenius equation as follows:

$$\ln \frac{K_{r_2}}{K_{r_1}} = \frac{E_r}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where K_{r_1} and K_{r_2} are the calculated relative hydrolysis-time constants at the absolute temperatures T_1 and T_2 , respectively, and R = 1.986 cal. per degree per mole.

No absolute significance may be attached to values of K_r or E_r calculated in the foregoing manner, and such data are not presented here for this reason. Nevertheless, such calculations provide an empirical approach whereby the relative accessibilities of different cellulose fine structures may be evaluated.

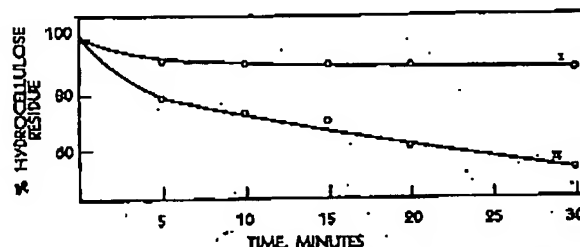


Figure 4. Comparison of Residual Weights Observed
In 2.50 *N* hydrochloric acid at 105° C.
I. Native cellulose (purified cotton)
II. Regenerated cellulose (viscose tire yarn)

LEVELING-OFF DEGREE OF POLYMERIZATION. Changes in degree of polymerization with time of hydrolysis in boiling 2.50 *N* hydrochloric acid for a native cellulose (purified cotton) and a regenerated cellulose (viscose tire yarn), respectively, are given in Table II and plotted in Figure 5.

In this connection, the author prefers to use the term "leveling-off degree of polymerization" in lieu of "limiting degree of polymerization" to refer to the relatively constant degree of polymerization reached after very prolonged mild conditions of hydrolysis or very short periods of drastic hydrolysis. If cellulose is hydrolyzed sufficiently it should be reduced to a true "limiting D.P." of 1.

PER CENT CRYSTALLINITY BY HYDROLYSIS. It is of particular interest to note from Figures 4 and 5 (1) how quickly the basic degree of polymerization reaches what appears to be a fairly constant value, (2) that this leveling off value is much higher for a native structure than for a regenerated structure, and (3) that a native structure loses weight with time of hydrolysis at a much slower rate than a regenerated structure. On the basis of these data, a time of 15 minutes in 2.50 *N* hydrochloric acid at the boil was arbitrarily adopted as being the optimum point at which to measure both weight loss on hydrolysis—i.e., per cent crystalline residue by hydrolysis—and the leveling-off degree of polymerization.

Weight loss and basic degree of polymerization data for all ten samples, after standard hydrolysis for 15 minutes in 2.50 *N* at the boil, are compiled in Table III. Whereas native structures show relatively small differences in residues at the end of

TABLE III. STANDARD WEIGHT LOSS DATA
(Using 2.5 N HCl at boil, 15 minutes)

No.	Sample	Original Basic D. P.	% Crystalline Residue	Leveling-off Basic D. P.
I	Purified cotton	3200	91.4, 91.8 91.0, 91.2	255, 260 242, 241
II	Bleached linters	1900	91.0	280
III	Linters pulp	880	91.9	285
IV	Wood pulp	1080	92.2	260
V	Avicel tire yarn	490	71.0, 71.0 70.4, 71.6	89, 44 45, 48
VI	Avicel textile yarn	470	76.4	55
VII	Experimental rayon (HST)	440	71.5	40
VIII	Experimental rayon (LST)	85	76.7	55
IX	Fortisan	460	90.6	85
X	Fiber G	560	87.0	6

TABLE IV. MILD AND DRASTIC HYDROLYSIS OF WOOD PULP

Time	5 N HCl, 18° C.		2.5 N HCl, Boil		5 N HCl, 18° C. Plus 2.5 N HCl, Boil	
	% Residue	D. P.	% Residue	D. P.	% Residue	D. P.
0	...	1080	...	1080	...	1080
1 min.	97.7	480
8 min.	98.1	862
5 min.	94.8	310
15 min.	90.8	290
24 hours	98.7	475	95.4	198
72 hours	98.7	416	95.1	188
150 hours	98.6	392	94.9	188
1 week	97.9	330	90.8	197
2 weeks	97.7	312	95.8	188
23 weeks	94.7	284
44 weeks	94.0	238	90.4	198
28-week sample washed repeatedly with 2.5 N HCl at boil	93.5	265

the hydrolysis, it is important to note the wide range of values obtained for the various samples possessing regenerated cellulose fine structures. The data in Table III illustrate further the high degree of reproducibility ($\pm 0.50\%$) possible in measuring the per cent crystalline hydrocellulose residues by hydrolysis, using the apparatus and method described.

CRYSTALLIZATION ON HYDROLYSIS. Experimental evidence in support of the crystallization-on-hydrolysis hypothesis was obtained by comparing the loss in weight under mild hydrolyzing conditions with the loss in weight under drastic conditions. These data are tabulated in Tables IV and V.

The data in Table IV show weight loss and degree of polymerization data for a rayon grade wood pulp which was subjected to (1) mild hydrolysis (5 N hydrochloric acid at 18° C.), (2) drastic hydrolysis (2.5 N hydrochloric acid 105° C.), and (3) mild plus drastic hydrolysis (5 N hydrochloric acid at 18° C. followed by 2.5 N hydrochloric acid 105° C.).

Parallel mild, drastic, and mild plus drastic hydrolysis data for a tire yarn made from the aforementioned rayon wood pulp are given in Table V, which shows that little or no loss in weight was found for the tire yarn after mild hydrolysis for relatively short periods of time. The slight gains in weight are not believed significant, as they are of the order of the experimental accuracy in measuring such weight losses. There is the possibility, however, that very small contributions to the weight of the cellulose residue may be made in view of the fact that a molecule of water is added to the cellulose molecules each time a 1,4 glycosidic bond is split.

In Table VI, the effect of a mild prehydrolysis treatment (10 days in 2.50 N hydrochloric acid at 18° C.) for ten different textile yarns is shown to increase markedly the per cent crystallinity by hydrolysis of these yarns.

The data shown in Tables IV, V, and VI appear to demonstrate that mild hydrolysis of cellulose induces crystallization with

little or no loss in weight. This is evidenced by the fact that, in all cases, the samples lost substantially less weight on being subjected to a standard drastic hydrolysis treatment after they had been subjected to a preliminary mild hydrolysis, than they did upon being given the standard drastic treatment directly. This effect is shown, however, to be far more pronounced in the case of regenerated cellulose than of native cellulose.

MECHANISMS FOR HETEROGENEOUS ACID HYDROLYSIS OF CELLULOSE FINE STRUCTURES

A schematic illustration of proposed mechanisms for the hydrolytic degradation of cellulose fine structure under both mild and drastic conditions of hydrolysis is presented in Figure 6.

This picture of the acid degradation of cellulose fine structure is capable of explaining all the data on degree of polymerization and weight loss which have been presented in this paper.

When hydrolysis conditions are relatively mild, the mechanism illustrated in Part A of Figure 6 is believed to apply. Under these conditions, only a small number of 1,4 glycosidic bonds of the accessible cellulose chains are split per unit time. This makes crystal growth possible, and longer segments of cellulose chains in the amorphous phase of the fine structure can "crystallize" before further chain splitting takes place, giving rise to a progressively less accessible fine structure.

However, when hydrolysis conditions are drastic, the mechanism illustrated in Part B of Figure 6 is more likely. Under these conditions, splitting of 1,4 glycosidic bonds proceeds so rapidly that substantially only very short segments of cellulose chains are available for "crystallization." In other words, relatively small, more hydrochloric acid-soluble areas are formed by drastic hydrolysis. Because the solubility of short-chain crystalline areas, formed simultaneously with drastic hydrolysis, should be appreciably greater than the solubility of longer "crystalline" components resulting from a slow splitting of 1,4 glycosidic bonds, one would expect a larger loss in weight with boiling hydrochloric acid, as was found.

Furthermore, if a fine structure which had been hydrolyzed in accordance with the mechanism illustrated in Part A of Figure 6 were subsequently subjected to drastic hydrolyzing conditions that would favor the mechanism proposed in Part B of Figure 6, we would expect the average leveling off basic degree of polymerization and the weight loss of the resulting hydrocellulose residue to be lower than if the mechanism illustrated in Part A had been by-passed, and that of Part B applied directly. Drastic

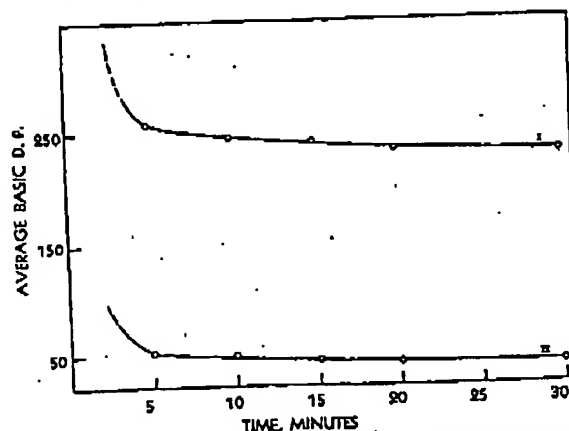


Figure 5. Variation in Basic Degree of Polymerization with Time of Hydrolysis

In 2.50 N hydrochloric acid at 105° C.
I. Native cellulose (purified cotton)
II. Regenerated cellulose (viscose tire yarn)

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TABLE V. MILD AND DRASTIC HYDROLYSIS OF EXPERIMENTAL TIRE YARN FROM WOOD PULP

Time	5 N HCl, 18° C.		2.5 N HCl, Boil		5 N HCl, 16° C. Plus 2.5 N HCl, Boil	
	% Residue	D. P.	% Residue	D. P.	% Residue	D. P.
0	..	496	..	496	..	496
1 min.	93.6	87
3 min.	87.8	81
5 min.	82.7	57
15 min.	71.0	35
24 hours	100.7	208	90.6	47
72 hours	100.8	119	85.6	43
120 hours	100.1	118	83.4	40
1 week	100.0	86	92.9	48
2 weeks	100.0	61	90.3	33
28 weeks	88.25	57
44 weeks	83.6	34	86.6	24
28-week sample washed repeatedly with 2.5 N HCl at boil	87.0	44

TABLE VI. EFFECT OF MILD ACID HYDROLYSIS ON CRYSTALLIZATION OF TEXTILE YARNS

No.	% Crystalline Residue (after 15 Min. 2.5 N HCl at Boil)		Average Basis D. P.		
	Before mild hydrolysis	After mild hydrolysis	Original yarn	After mild hydrolysis	After drastic hydrolysis ^b
I	77.1	87.3	425	91	46
II	80.2	88.8	425	88	47
III	81.7	86.2	425	88	48
IV	82.4	87.8	429	88	48
V	83.0	88.8	433	91	48
VI	83.7	88.9	432	94	48
VII	82.8	88.0	429	93	48
VIII	82.8	87.7	415	95	46
IX	82.8	84.3	419	92	46
X	83.9	89.5	422	91	50

^a Mild hydrolysis, 10 days in 2.5 N HCl at 18° C.^b Drastic hydrolysis, 15 min. in 2.5 N HCl at 105° C. (boil).

hydrolysis alone (Part B) should remove very short-chain fragments which would otherwise act to lower the average basic degree of polymerization of the residue, whereas in the case of mild hydrolysis followed by drastic hydrolysis crystallized short-chain material would be retained in the residue, tending to lower its average basic degree of polymerization. In other words, the distribution of crystalline particle sizes in the residue of a given sample after mild hydrolysis would be different from the distribution of crystalline particle sizes in the residue after drastic hydrolysis.

CONCLUSIONS

The weight loss on hydrolysis is shown to be dependent on a combination of (1) the rate at which hydrolysis proceeds, and (2) crystallization and crystal growth which appear to occur simultaneously with the hydrolysis. When mild hydrolyzing conditions are used for long periods of time, much smaller losses in weight are found than when drastic conditions of hydrolysis are used for short periods of time, even though the average degree of polymerization approaches the same leveling-off values in each case. Furthermore, mild hydrolyzing pretreatments which favor crystallization of disorganized and strained chains are found to be effective in reducing sharply the weight lost upon subsequent drastic hydrolysis.

The results are explained by assuming that mild hydrolyzing conditions, during which 1,4 glycosidic bonds are split at a relatively slow rate, favor crystal growth and the crystallization of long-chain segments which are acid insoluble and resistant to further rapid hydrolysis. Drastic hydrolysis, on the other hand, during which available 1,4 glycosidic bonds are split rapidly, results in the crystallization of very-short-chain segments, giving rise to crystalline nuclei which are acid soluble and more readily removed during the hydrolysis.

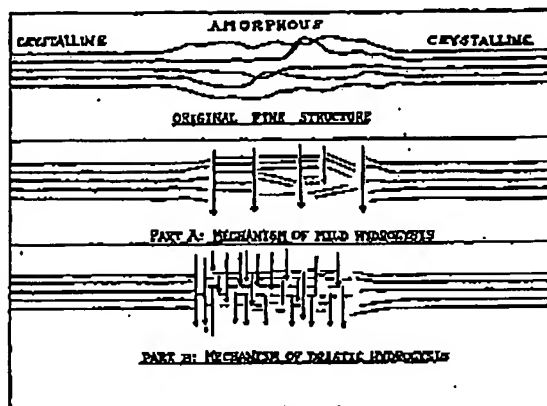


Figure 6. Schematic Representation of Mild and Drastic Hydrolysis of Cellulose

The foregoing crystallization-on-hydrolysis effects are found to be much more pronounced with regenerated celluloses than with native celluloses.

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